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SYNTHESIS AND PROPERTIES OF AROMATIC POLYIMIDES CONTAINING THE SIX-MEMBERED RING SYSTEM

*POLYMER BRANCH
NONMETALLIC MATERIALS DIVISION*

JUNE 1976

TECHNICAL REPORT AFML-TR-76-27
FINAL REPORT FOR PERIOD MARCH 1973 to APRIL 1974

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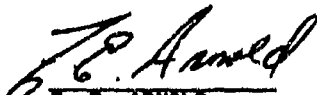
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This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Subtask No. 73400403, "Synthesis of Novel Polymer Materials for High Temperature Resin Applications." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the AFML Project Scientist. This report describes work conducted from March 1973 to April 1974.

This report has been reviewed by the Information Office (IO) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.


F. E. ARNOLD
Project Scientist

FOR THE COMMANDER


R. L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This work was performed to determine the best synthetic procedure for the preparations of six-membered polyimides, and the extent to which processability parameters such as solubility and fusibility could synthetically be altered in the polymer system. The six-membered imide ring system has excellent hydrolytic stability in highly corrosive solvents, both acidic and basic; however, the system has not been prepared in high molecular weight due to the 'perc' effect of the dianhydride monomers.			

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A number of new arylenoxy and arylenethio-bis-'pere' anhydrides have been synthesized for use as monomers for the preparation of soluble and fusible polyimides containing six-membered rings. The bis-anhydrides were converted to polyimides by solution polycondensation with oxyarylenediamines. The polyimides were soluble in m-cresol and exhibited glass transition temperatures in the 260-360°C range. All of the polymers displayed good thermal and thermal oxidative properties; although high molecular weights were not achieved.

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FOREWORD

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The work described in this report was conducted in the Polymer Branch Laboratory by G. A. Loughran of the Air Force Materials Laboratory and F. E. Arnold. The manuscript was released by the authors in December 1974 for publication as a technical report.

The authors wish to thank Dr. G. F. L. Ehlers and Mr. K. R. Fisch for the determination of glass transition temperatures and isothermal aging studies of the polymers.

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SECTION I

INTRODUCTION

Aromatic polyimides possessing the common five-membered benzimide ring system have been extensively investigated in both industrial and government laboratories. The investigations have resulted in a large number of structure property correlations and also a variety of different commercial products for both adhesive and composite applications. Six-membered ring polyimides possessing naphthalimide structures, on the other hand, have received little attention primarily due to the inability of obtaining soluble precursors for fabrication.

Previous work on six-membered polyimides have shown that the polymer system exhibits excellent thermal and thermal oxidative stability as evidenced by thermal gravimetric analysis (Reference 1) and isothermal aging studies (Reference 2). The six-membered imide ring system has also been shown to exhibit excellent hydrolytic stability in highly corrosive basic and acidic media (References 3 and 4).

The objective of this work is to investigate the synthesis of polyimides with six-membered rings in an effort to obtain high molecular weight materials. With high molecular weights, a meaningful comparison between the six-membered and five-membered polyimide system could be obtained with respect to their physical, mechanical, and environmental properties. It is a further objective to determine the extent to which processability parameters such as solubility and fusibility could synthetically be altered in the six-membered polyimide system.

SECTION II

DISCUSSION OF RESULTS

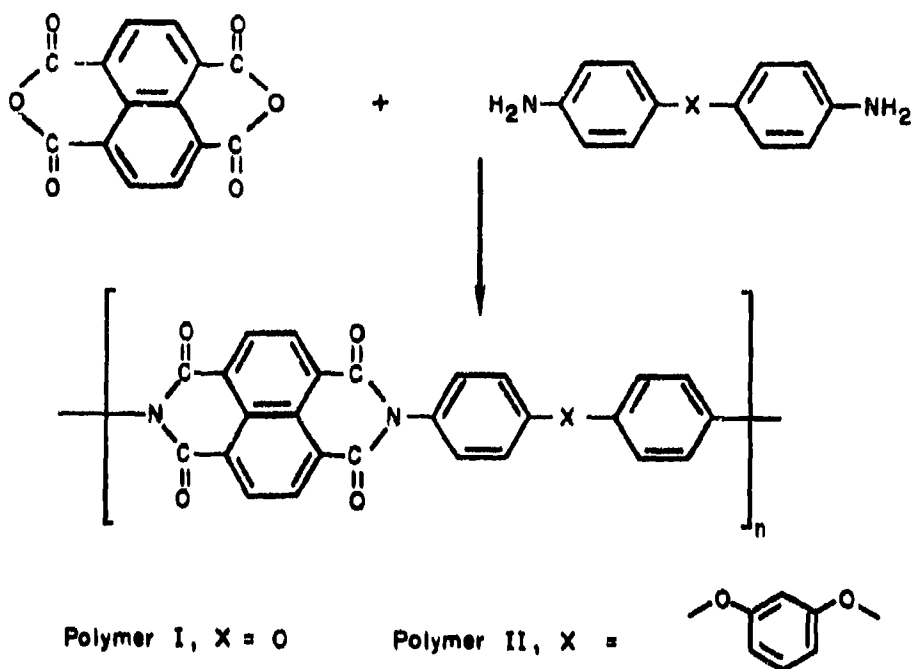
1. POLYMERIZATION STUDIES

a. Polymers for the polycondensation of equimolar quantities of oxydianiline, or 1,3-di-(3-aminophenoxy)benzene and 1,4,5,8-naphthalene-tetracarboxylic anhydride.

Since low molecular weight polymers were obtained by prior workers (References 1 and 2) when 4,4'-oxydianiline and other aromatic diamines were reacted with 1,4,5,8-naphthalenetetracarboxylic dianhydride in solution in N,N-dimethylacetamide, a number of different methods were tried in order to obtain higher molecular weights. It is well known that polyphosphoric acid is ineffective because low molecular weight products precipitate from the reaction mixture. These polymers also precipitate from DMAC and DMSO.

Our investigations began with the use of phenyl sulfone as a solvent in the preparation of poly[1,3,6,8-tetrahydro-1,3,6,8-tetraoxobenzo(1,m,n)(3,8) phenanthroline-2,7-diyl)-p-phenyleneoxy-p-phenylene] (I), and poly[1,3,6,8-tetrahydro-1,3,6,8-tetraoxobenzo(1,m,n)(3,8)phenanthroline-2,7-diyl)-m-phenyleneoxy-m-phenyleneoxy-m-phenylene (II), from the polycondensation of 4,4'-oxydianiline or 1,3-di(3-aminophenoxy)benzene respectively with 1,4,5,8-naphthalenetetracarboxylic dianhydride. Low molecular weight polymers, I and II, were obtained when a reaction temperature of 379°C was used and viscosities no higher than $\eta_{inh} = 0.15$ could be obtained. Lowering the reaction temperature to 200°C resulted in no significant improvement. In both cases the products were difficult to purify and characterize.

Next, a mixture of m-cresol (2) and benzene (1) was used as a solvent medium for the polycondensation reactions, at a polymer concentration of 2%. Water produced during the reaction was removed azeotropically.



Best results were obtained when the reactions were carried out at 120°C for 18 hours under nitrogen followed by further heating for 24 hours. Polymer I was obtained with an inherent viscosity, η_{inh} as high as 0.33/0.5%/H₂SO₄. When the method was used for the polycondensation of 1,3-di(3-aminophenoxy)benzene and 1,4,5,8-naphthalenetetracarboxylic dianhydride, the resulting polymer, II, had an inherent viscosity $\eta_{\text{inh}} = 0.20$.

A study of polyimide formation in the reaction of pyromellitic dianhydride and other aromatic dianhydrides with certain aromatic diamines in aprotic solvents, such as N,N-dimethylacetamide and dimethylsulfoxide (References 5, 6, and 7) reveals that limitation in molecular weight is directly related to the nucleophilicity of the solvent and to the degree of stability of the charge-transfer complex formed between the electrophilic dianhydride and the nucleophilic solvent.

Subsequent reaction of this charge-transfer complex with the diamine produces a new charge-transfer complex which is much less stable, and transfer of one of the free mobile protons at the diamine results in formation of the amide bond. Through such a process the polyamic acid molecule is built up. The reaction only proceeds at a high rate and to a high degree of conversion when the charge-transfer complex is quite unstable. It has been found that this can occur when the reaction is carried out in m-cresol containing a tertiary amine such as pyridine, quinoline, or isoquinoline as catalyst (Reference 8). The greater the electron donor capacity of the nitrogen atom of the heterocyclic ring of the catalyst, the higher the molecular weight attained. More recently Levine, in a study of the polycondensation of 4,4'-diaminodiphenylmethane and 1,5-cyclooctadiene-1,2,5,6-tetracarboxylic dianhydride, obtained low molecular weight polymers, with inherent viscosities not greater than 0.15, when N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, or N-methyl pyrrolidine (Reference 9) were used as solvents. He was able to obtain polymers with high viscosities, i.e. $\eta = 1.3 - 1.9$, by running the reactions in m-cresol containing isoquinoline as catalyst.

Therefore, it became desirable to study the polycondensation of 4,4'-oxydianiline and 1,4,5,8-naphthalenetetracarboxylic dianhydride under similar conditions. A number of reactions were run in m-cresol using either quinoline at a polymer concentration of 2% or isoquinoline at a polymer concentration of 10%. Significant improvement in molecular weight was realized and polymers with intrinsic viscosities up to $\eta = 0.57$ could be obtained by the method. Those prepared at 2% concentration in m-cresol were soluble and remained in solution; however, reactions carried out at 10% concentrations resulted in precipitation of the polymer.

b. Polymer from the polycondensation of equimolar quantities of 4,4'-oxydianiline and 1,2,4,5-naphthalenetetracarboxylic dianhydride.

The polycondensation of 4,4'-oxydianiline and 1,2,4,5-naphthalenetetracarboxylic dianhydride was tried in m-cresol containing quinoline to see if a modification in structure would sufficiently change the "pore effect" to allow for a significant increase in molecular weight. The resulting polymer, poly[8,10-dihydro-4,6,8,10-tetraoxobenzo[de]pyrrolo[3,4-g]isoquinoline-5,9(4H,6H)-diyl)-p-phenyleneoxy-p-phenylene] (III), is a mixed polyimide containing both six- and five-membered imide rings. Although its molecular weight was substantial with an inherent viscosity, η_{inh} 0.45, no dramatic increase was observed.

A tabulation of viscosity and glass transition temperature T_g data is given in (Table 1) for Polymers I, II, and III. The reaction conditions and resulting viscosities were the best obtained for the three polymers. T_g data of each polymer was obtained by one or more of the following techniques; differential scanning calorimetry (DSC), thermochemical analysis (TMA) or torsion braid analyses (TBA).

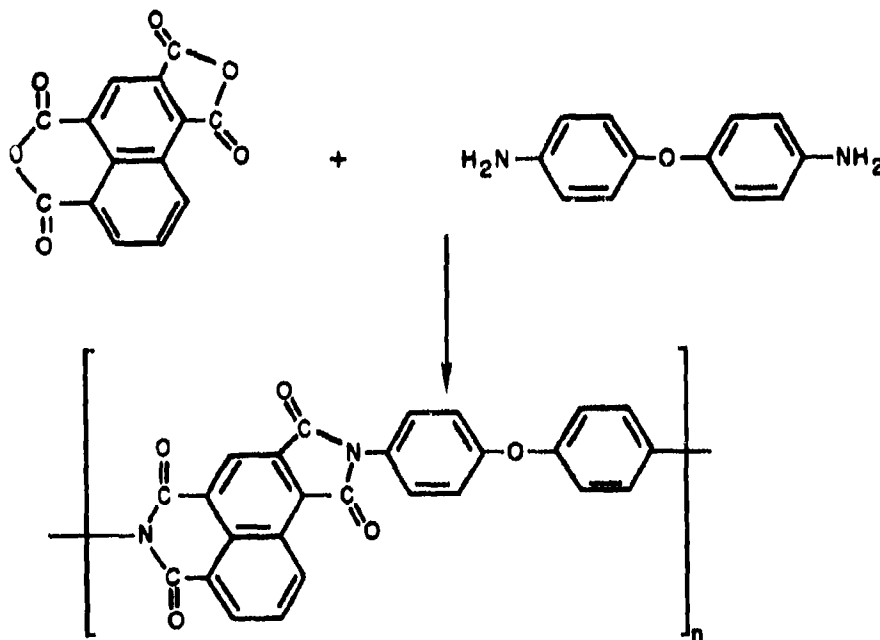
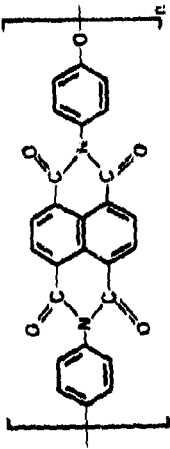
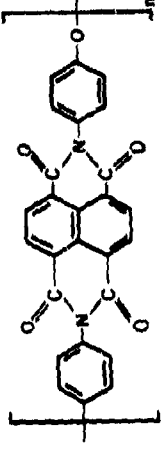
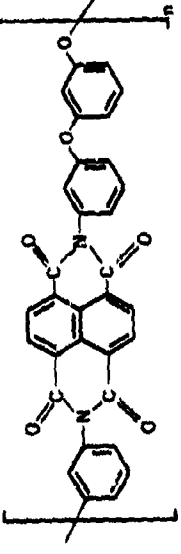
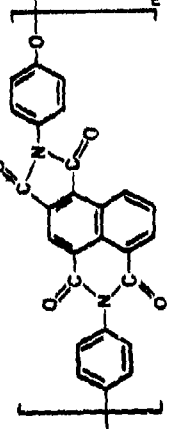


TABLE 1
COMPARISON OF PHYSICAL PROPERTIES OF POLYMERS I, II, AND III

SOLVENT	CATALYST	TEMP °C	TIME HRS	STRUCTURE OF POLYMER	VISCOSITY	T _g
m-cresol	quinoline	120°	18		0.42	336°
m-cresol	quinoline	120° 200°	18 24		0.56	336°
m-cresol benzene	none	120°	18		0.20	211°
m-cresol	quinoline	120° 200°	18 24		0.45	366°

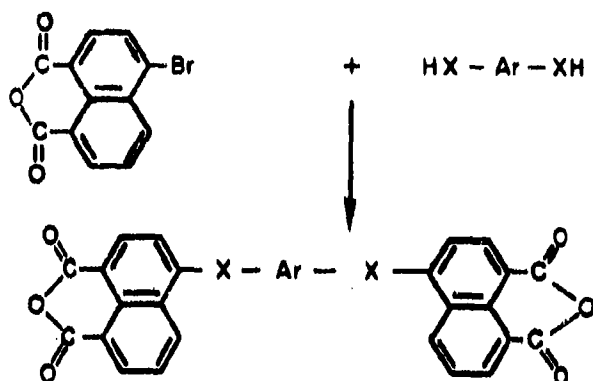
The thermal properties of Polymers I, II, and III are depicted in Figure 1 (thermal gravimetric analysis) and Figure 2 (isothermal aging analysis).

2. STRUCTURAL TAILORING OF IMIDE SYSTEM

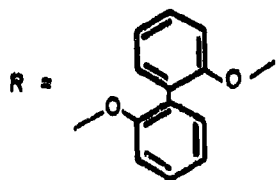
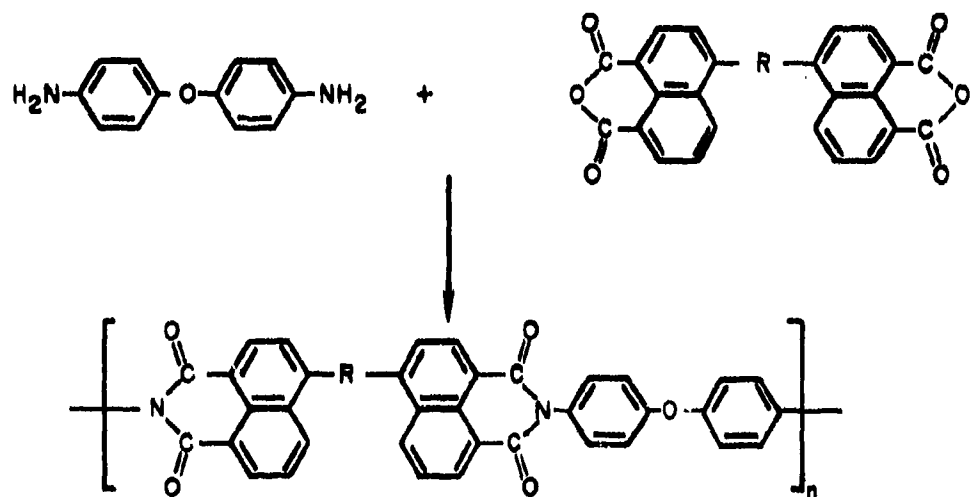
A series of new oxy and thioarylene bis-'pere' anhydrides were prepared in an effort to increase the extent of solubility in m-cresol and also to obtain more flexible polymer backbones for lower glass transition temperatures. The new monomers were prepared by the nucleophilic substitution of various aryl diols and bisthiols with 4-bromonaphthalic anhydride in N,N-dimethylacetamide. The metallic salts of the bis-nucleophiles were prepared in situ using sodium hydroxide in a mixture of DMAC and benzene. The water produced was removed azeotropically with subsequent addition of the 4-bromo-1,8-naphthalicanhydride. A more convenient method employed the use of potassium-t-butoxide in a dry tetrahydrofuran solution containing the diol or bisthiol. Removal of the solvent provided the dry dipotassium salts as solids. Addition of a solution of 4-bromo-1,8-naphthalicanhydride in dry DMAC resulted in a smooth displacement of the bromine and gave good yields of the desired bis-'pere' anhydrides. The melting points of the new monomers prepared are listed in Table 2 and their infrared spectra shown in Figures 3-7.

The polycondensations were carried out at a 10% polymer concentration in m-cresol using isoquinoline as catalyst. In contrast to the behavior of the more rigid Polyimide I, which precipitated from m-cresol at this concentration, all of the new polymers remained soluble. The molecular weights of the polymers were low with viscosities in 0.1 to 0.3 range (Table 3).

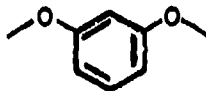
The glass transition temperatures (Table 3) for the polymers were in the 250-270°C range, except for one at 362°C. This is considerably lower than 336°C for Polymer I. The exception was Polymer VIII which exhibited two Tgs, one at 317°C and the other at 362°C. Similar behavior



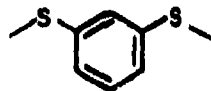
Five different bis-'pere' anhydrides were condensed with 4,4'-oxydianiline to give Polymers IV - VIII.



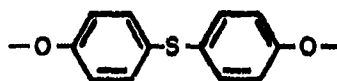
Polymer IV



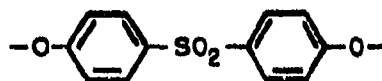
Polymer V



Polymer VI



Polymer VII



Polymer VIII

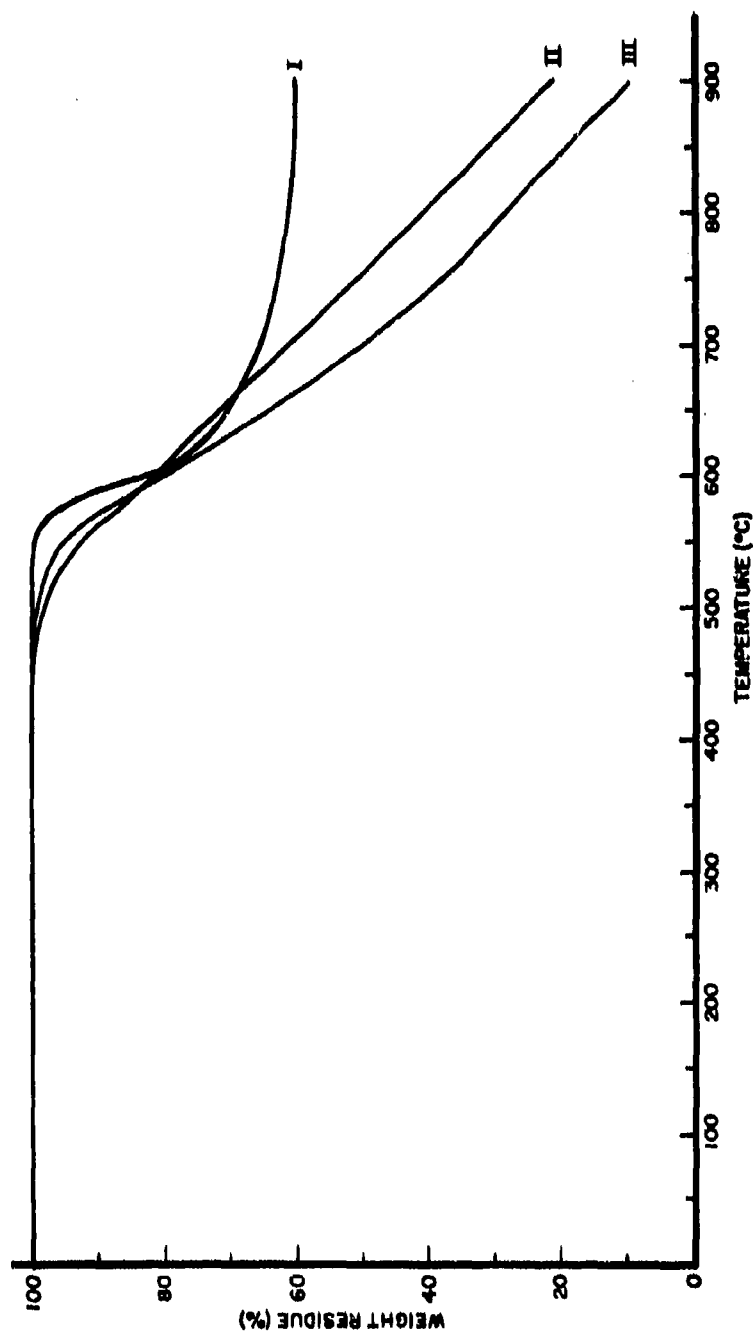


Figure 1. Thermal Gravimetric Analysis of Polymers I, II, and III (H_2)

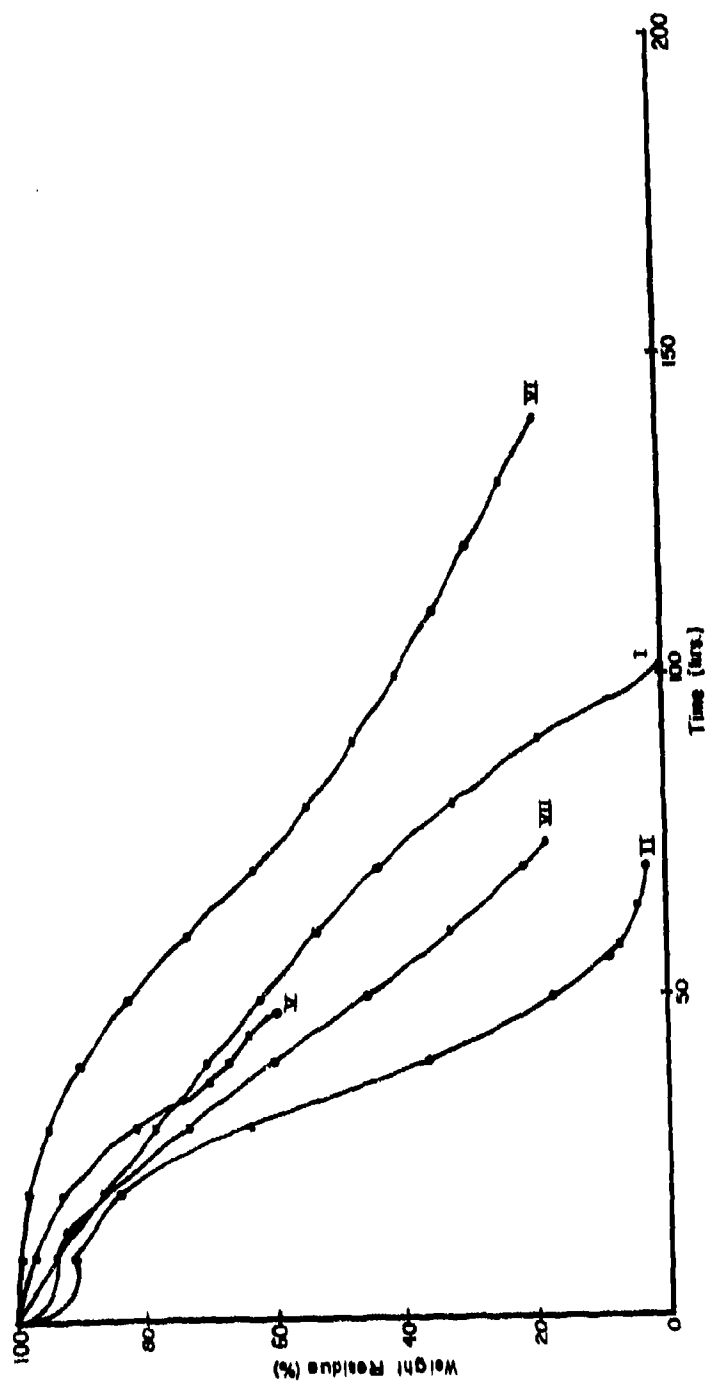


Figure 2. Isothermal Aging Curves of Polymers I, II, V, VI, and VII in Air at 730°F

TABLE II
'PERE' ANHYDRIDE MONOMERS

STRUCTURE	m.p. °C
The structure shows two phthalic anhydride units connected by two phenyl rings. Each phthalic anhydride unit is attached to a phenyl ring at the para position, and the two phenyl rings are connected to each other at their para positions.	287
The structure shows two phthalic anhydride units connected by a single phenyl ring. Each phthalic anhydride unit is attached to the phenyl ring at the para position.	272
The structure shows two phthalic anhydride units connected by a single phenyl ring. Each phthalic anhydride unit is attached to the phenyl ring at the para position via a sulfur atom.	223
The structure shows two phthalic anhydride units connected by a biphenyl group. Each phthalic anhydride unit is attached to one of the phenyl rings of the biphenyl group at the para position.	275
The structure shows two phthalic anhydride units connected by a 4,4'-biphenylene group. Each phthalic anhydride unit is attached to one of the phenyl rings of the biphenylene group at the para position.	>300

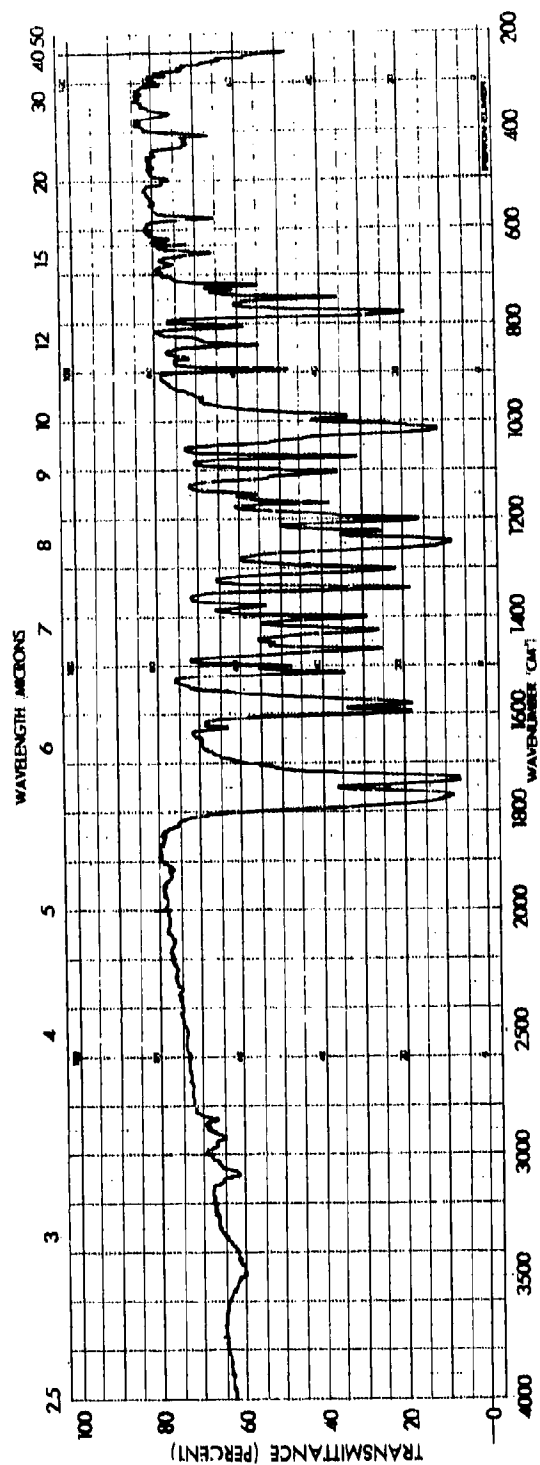


Figure 3. Infrared Spectrum of 2,2'-Bis(4-oxy-1,8-naphthalic anhydride)biphenyl

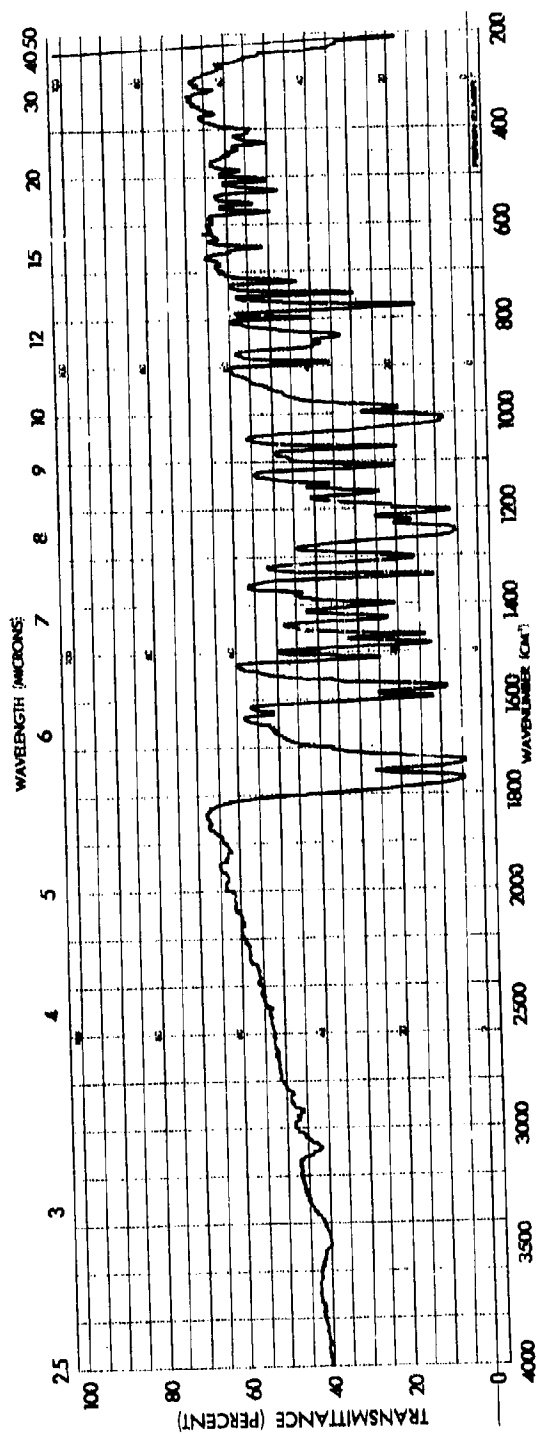


Figure 4. Infrared Spectrum of 4,4-Bis(4-oxy-1,8-naphthalic anhydride)diphenylsulfide

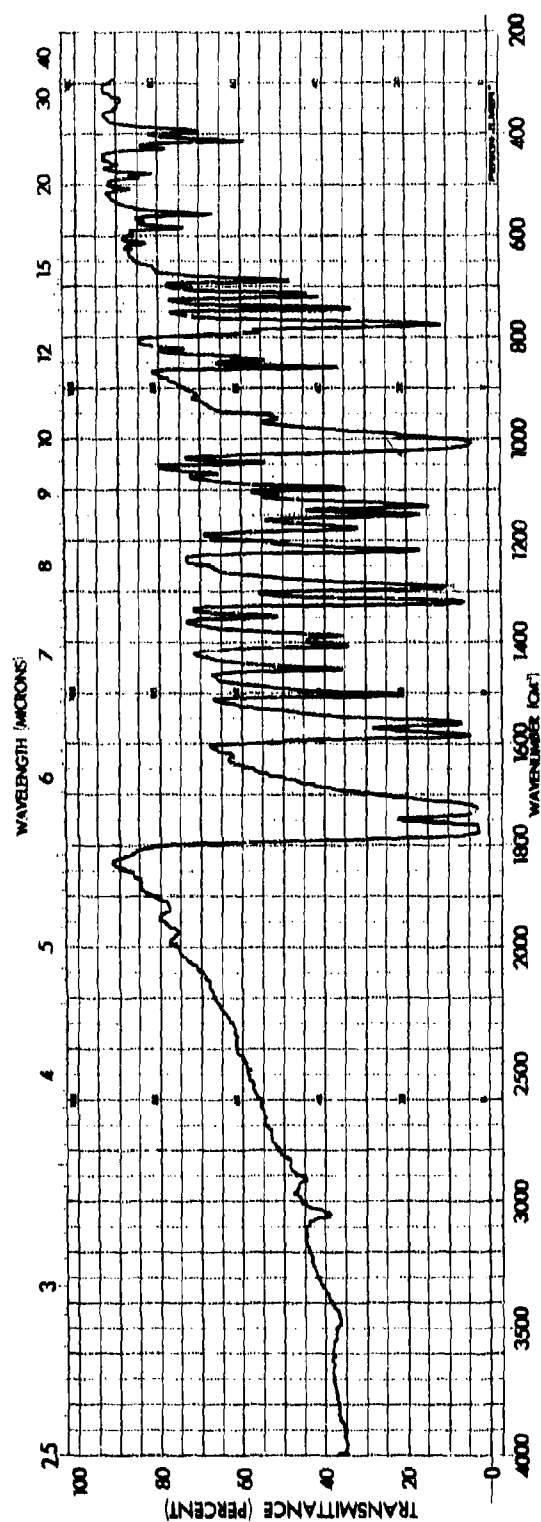


Figure 5. Infrared Spectrum of 1,3-Bis(4-thio-1,8-naphthalic anhydride)phenylene

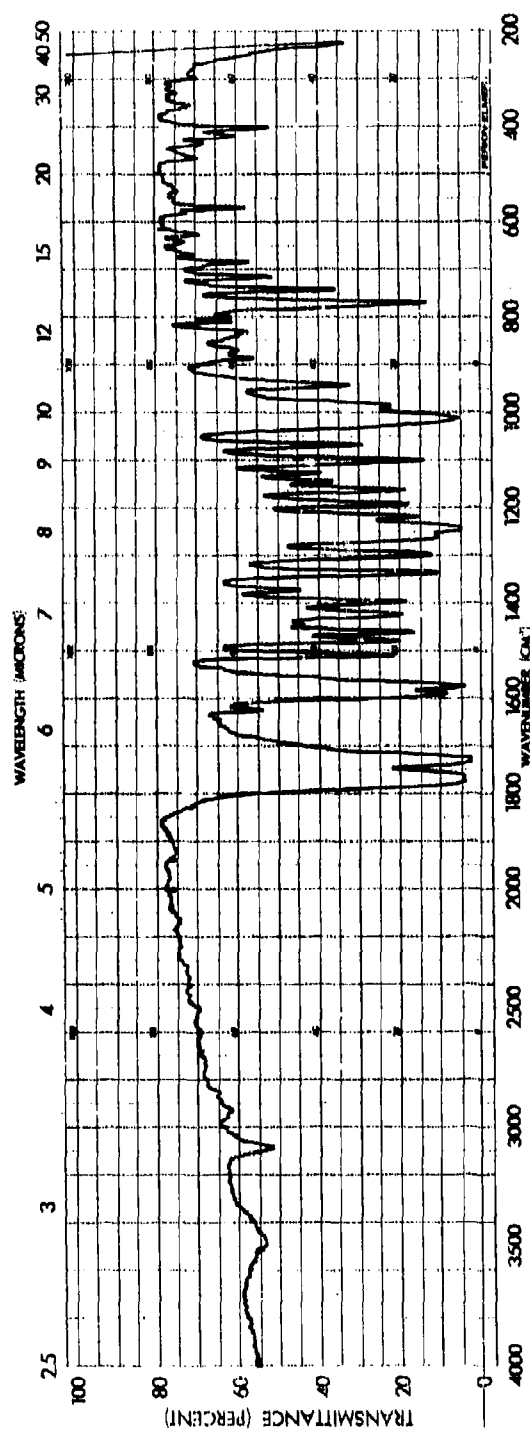


Figure 6. Infrared Spectrum of 1,3-Bis(4-oxy-1,8-naphthalic anhydride)phenylene

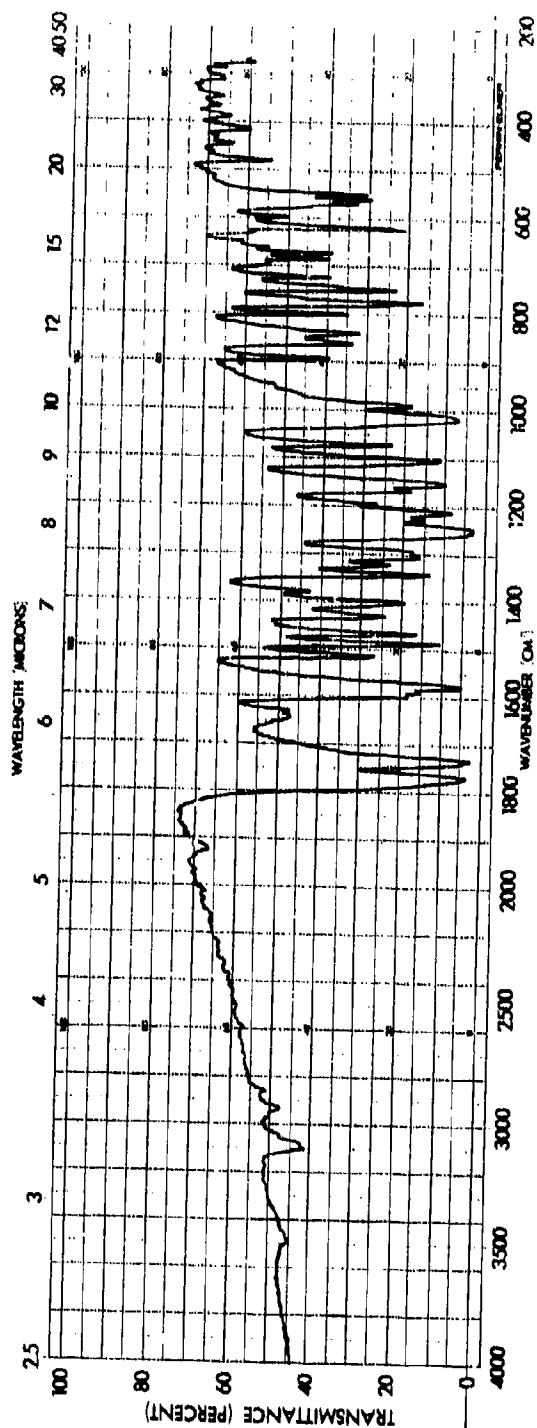
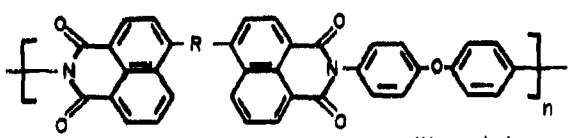
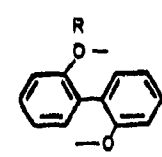
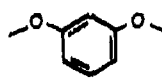
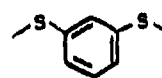
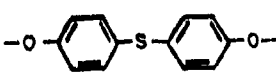
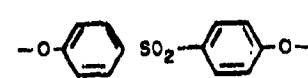


Figure 7. Infrared Spectrum of 4,4'-Bis(4-oxy-1,8-naphthalic anhydride)diphenyl sulfone

TABLE 3

GLASS TRANSITION TEMPERATURES OF SIX-MEMBERED
POLYIMIDES CONTAINING OXY AND THIO-ARYLENE GROUPS

	Polymer	Viscosities	Tg°C
	IV	0.15	260°
	V	0.20	260°
	VI	0.26	253°
	VII	0.30	269°
	VIII	0.29	317° Major & 362° Minor

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has been observed with certain other polyimides by Gilham (Reference 10) and have been explained as due to discrete modes of submolecular motion. The thermal properties of the polymers are compared with Polymers I - III and are shown in Figures 2 and 8.

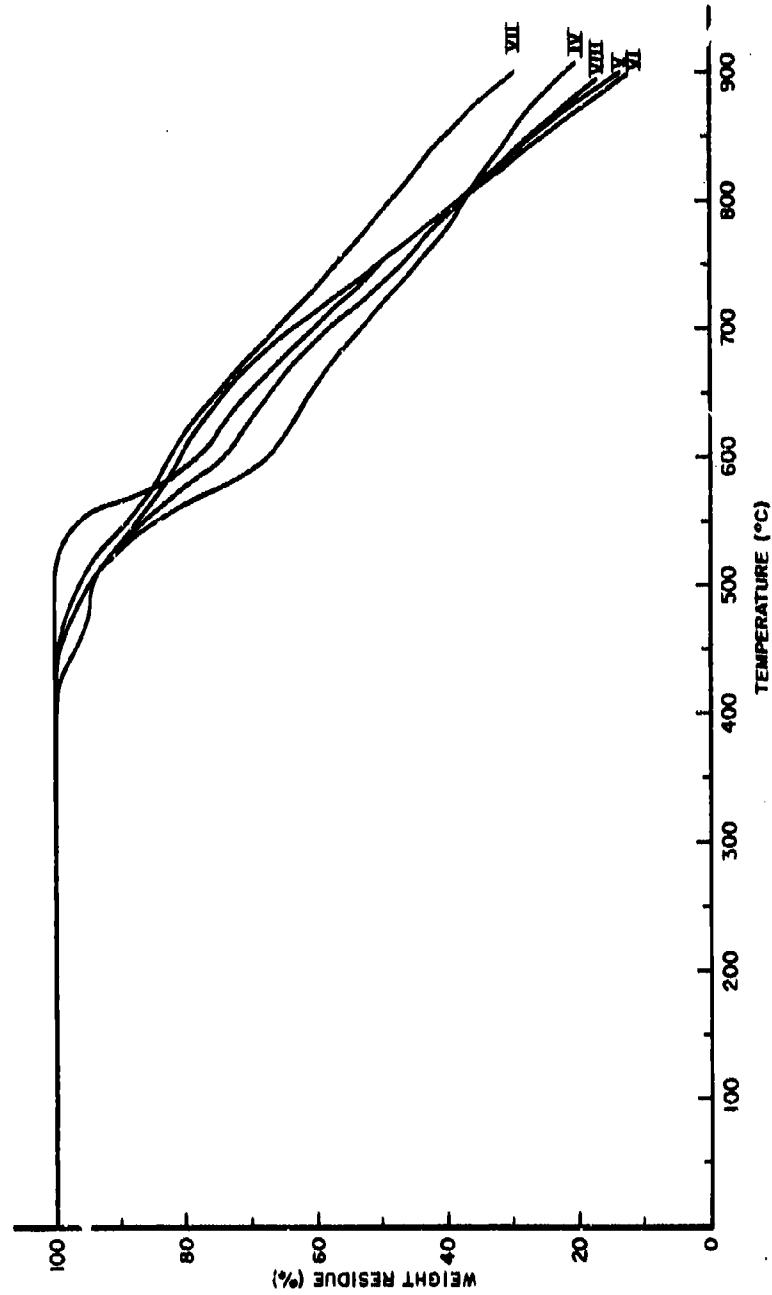


Figure 8. Thermal Gravimetric Analysis of Polymers IV, V, VI, VII, and VIII (N_2)

SECTION III

EXPERIMENTAL

1. NOMOMERS

- a. 1,4,5,8-Naphthalenetetracarboxylic acid dianhydride
(Celanese Research Company) was analyzed and used as received.

- b. 1,2,4,5-Naphthalenetetracarboxylic acid dianhydride

The monomer was prepared from 2-acetonaphthalene-1,4,5-tricarboxylic acid anhydride by oxidation in aqueous alkaline sodium hypochlorite, m.p. 262-263°C (Reference 11).

Oxydianiline was obtained from Eastman Organic Chemicals and was purified by vacuum sublimation, m.p. 186-187°C.

- c. 1,3-Di-(3-aminophenoxy)benzene

Midwest Research Institute was analyzed and used as received.

- d. 2,2'-Bis(4-oxy-1,8-naphthalic anhydride)biphenyl

To a solution containing 2.32 g (0.0125 mole) of o,o'-dihydroxy-biphenyl in 150 ml of N,N'-dimethylacetamide was added, under a nitrogen atmosphere, 10 ml of a 10% aqueous solution of sodium hydroxide solution. The mixture was heated to 80°C and a solution of 6.93 g (0.025 mole) of 4-bromo-1,8-naphthalic anhydride dissolved in 150 ml of benzene was added dropwise over a one-hour period as the temperature rose to 100°C and water was removed as an azeotrope. The benzene was removed after eight hours, and the reaction mixture was precipitated into water to give an orange solid which was collected and dried at room temperature. The product was recrystallized from p-dioxane to give 6.9 g (95%), m.p. 287.5-287.6°C, I.R. spectra (Figure 3).

Analysis-Calcd for $C_{36}H_{18}O_8$ (percent): C, 74.73; H, 3.14
Found (percent): C, 74.67; H, 3.21

e. 4,4'-Bis(4-oxy-1,8-naphthalic anhydride)diphenylsulfide

To a solution containing 1.92 g (0.02 mole) of potassium-t-butoxide in 200 ml of tetrahydrofuran was added, under a nitrogen atmosphere, 2.18 g (0.01 mole) of 4,4'-dihydroxydiphenyl sulfide to give the dipotassium salt of the diol as a white precipitate. A solution containing 5.54 g (0.02 mole) of 4-bromonaphthalic acid dianhydride dissolved in 200 ml of N,N'-dimethylacetamide was added and the tetrahydrofuran was removed by distillation. The reaction mixture was refluxed for six hours and the solvent removed under reduced pressure. The residual solid was recrystallized from 200 ml of chlorobenzene to give 5.9 g (96.7%) of product melting at 274.4-275.4°C, I.R. spectra (Figure 4).

Analysis-Calcd for $C_{36}H_{18}O_8S$ (percent): C, 70.81; H, 2.97; S, 5.25

Found (percent): C, 70.69; H, 2.85; S, 5.36

f. 1,3-Bis(4-thio-1,8-naphthalic anhydride)phenylene

To a solution of 1.92 g (0.02 mole) of potassium-t-butoxide in 100 ml of tetrahydrofuran was added, under a nitrogen atmosphere, 1.42 g (0.01 mole) of m-benzenedithiol. To this solution was then added dropwise a solution of 5.54 g (0.02 mole) of 4-bromonaphthalic acid anhydride in 200 ml of N,N'-dimethylacetamide to give a brown liquid which changed to a clear amber liquid upon complete addition of the anhydride. The reaction mixture was heated and stirred under a nitrogen atmosphere as the tetrahydrofuran was removed by distillation. The reaction mixture was heated to 150°C and maintained at that temperature for six hours. After cooling to room temperature, the inorganic salts were removed by filtration and the solvent in the filtrate was removed under reduced pressure. The residual gummy tan residual was recrystallized from dioxane with charcoal treatment and dried under reduced pressure to give 4.0 g (75%) yield, m.p. 222.5-223°C, I.R. spectra (Figure 5).

Analysis-Calcd for $C_{30}H_{14}O_6S_2$ (percent): C, 67.41; H, 2.64; N, 12.00

Found (percent): C, 67.15; H, 2.62; N, 11.98

g. 1,3-Bis(4-oxy-1,8-naphthalic anhydride)phenylene

To a solution of 1.10 g (0.01 mole) of resorcinol in 50 ml of anhydrous benzene was added 1.04 g (0.02 mole) of sodium methoxide. The solution was stirred at room temperature for one hour and 5.52 g (0.02 mole) of 4-bromonaphthalic acid dianhydride dissolved in 100 ml of N,N'-dimethylacetamide was added. The reaction mixture was heated to 80°C to remove the benzene and then slowly heated to 150°C and maintained at that temperature for six hours. The cooled solution was poured over ice to precipitate a light yellow solid. The bis-dianhydride was collected, washed with water, dried under reduced pressure, and recrystallized from acetone to afford 4.10 g (81.6%) m.p. 271-272°C, I.R. spectra (Figure 6).

Analysis-Calcd for $C_{30}H_{14}O_8$ (percent): C, 71.71; H, 2.80

Found (percent): C, 71.63; H, 2.69

h. 4,4'-Bis(4-oxy-1,8-naphthalic anhydride)diphenylsulfone

To a solution containing 3.13 g (0.0125 mole) of 4,4'-dihydroxydiphenyl sulfone in 150 ml of N,N'-dimethylacetamide was added, under a nitrogen atmosphere, 10 ml of a 10% aqueous sodium hydroxide solution. The mixture was heated to 80°C, and a solution of 6.93 g (0.025 mole) of 4-bromo-1,8-naphthalic anhydride dissolved in 200 ml of toluene was added dropwise over a one-hour period as the temperature rose to 100°C and water was removed as an azeotrope. The toluene was removed after eight hours, and the reaction mixture was precipitated into water to give a yellow solid which was collected and dried at 160°C/40 mm. The product was recrystallized from N,N'-dimethylacetamide to give 7.5 g (93%), m.p. > 300°C, I.R. spectra (Figure 7).

Analysis-Calcd for $C_{36}H_{18}O_{10}S$: C, 67.28; H, 2.82; S, 4.99

Found (percent): C, 67.03; H, 2.70; S, 5.15

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2. POLYMERS

- a. Poly[(1,3,6,8-tetrahydro-1,3,6,8-tetraoxobenzo[1,m,n][3,8]phenanthroline-2,7-diyl)-p-phenyleneoxy-p-phenylene] (I)

A mixture of 0.5006 g (0.0025 mole) of oxydianiline, 0.6704 g (0.0025 mole) of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride and 0.96 g (0.005 mole) of quinoline were heated under a nitrogen atmosphere for 18 hours at 120°C followed by an additional 24 hours at 200°C. The reaction mixture was cooled to room temperature and poured into 500 ml of methanol. The polymer was collected, washed with methanol, and dried under reduced pressure at 120°C/1 mm to give 1.0 g (92%) yield. The polymer had an inherent viscosity of 0.56 dl/gm in sulfuric acid (0.50 g/100 ml at 30°C).

Analysis Calc'd for $C_{26}H_{12}O_5N_2$: C, 71.71; H, 3.23; N, 6.27

Found : C, 71.12; H, 2.70; N, 6.16

- b. Poly[(1,3,6,8-tetrahydro-1,3,6,8-tetraoxobenzo[1,m,n][3,8]phenanthroline-2,7-diyl)-m-phenyleneoxy-m-phenyleneoxy-m-phenyleneoxy-m-phenylene] (II)

To 60 ml of m-cresol containing 30 ml of anhydrous benzene was added 5846 g (0.002 mole) of 1,3-di(3-aminophenoxy)benzene, and 0.5363 g (0.002 mole) of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride. The mixture was heated to 120°C and the water of condensation was distilled off azeotropically with the benzene. After 24 hours at 120°C the reaction mixture was then allowed to cool to 30°C and the polymer precipitated into 500 ml of methanol. The resulting brown polymer was collected, washed with methanol, and dried under reduced pressure at 120°C/1 mm to give 0.95 g (96%) yield. The polymer had an inherent viscosity of 0.20 in m-cresol (0.5 g/100 ml at 30°C).

Analysis Calc'd for $(C_{32}H_{16}O_6N_2)_n$: C, 73.28; H, 3.08; N, 5.34

Found: C, 71.99; H, 3.05; N, 4.80

- c. Poly[(8,10-dihydro-4,6,8,10-tetraoxobenzo[de]pyrrolo[3,4-g]isoquinoline-5,9(4H,6H)diyl)-p-phenyleneoxy-p-phenylene] (III)

To 50 ml of m-cresol containing one ml of quinoline was added, under a nitrogen atmosphere, 0.500 g (0.0025 mole) of oxydianiline and 0.6704 g (0.0025 mole) of 1,2,4,5-naphthalenetetracarboxylic acid dianhydride. The mixture was heated to 120°C and maintained at that temperature for 18 hours. The temperature was then increased to 200°C and maintained at that temperature for 24 hours. The polymer was isolated by pouring the cooled reaction mixture into 500 ml of methanol, washing with methanol, and drying under reduced pressure at 120°C/1 mm. The polymer 0.95 g (88%) had an inherent viscosity of 0.45 in sulfuric acid (0.5 g/100 ml at 30°C).

Analysis Calc'd for $(C_{25}H_{12}O_5N_2)_n$: C, 72.22; H, 3.23; N, 6.27

Found: C, 69.17; H, 2.70; N, 6.25

- d. Poly[(1,3-dioxo-1H-benz[de]isoquinoline-2,6(3H)-diyl)oxy-2,2'-biphenyleneoxy(1,3-dioxo-1H-benz[de]isoquinoline-6,2(3H)-diyl)-p-phenyleneoxy-p-phenylene] (IV)

A solution containing 0.641 g (0.0032 mole) oxydianiline, 1.84 g (0.0032 mole) of 2,2'-bis(4-oxy-1,8-naphthalic anhydride)-biphenyl, and 0.18 g of isoquinoline dissolved in 25 ml of m-cresol was heated, under a nitrogen atmosphere, at 180-200°C for 20 hours. The reaction mixture was cooled to room temperature and the polymer was precipitated into 1.5 liters of methanol. The polymer was collected and washed several times with methanol and air-dried to give 2.3 g (99%). The polymer had an inherent viscosity of 0.15 dl/g in sulfuric acid (0.5 g/100 ml at 30°C). The polymer exhibited a glass transition, T_g , at 260°C by Differential Scanning Calorimetry (DSC).

Analysis-Calc'd for $(C_{48}H_{26}O_7N_2)_n$ (percent): C, 77.62; H, 3.53; N, 3.77

Found (percent): C, 72.20; H, 3.08; N, 3.56

- e. Poly[(1,3-dioxo-1H-benz[de]isoquinoline-2,6(3H)-diyl)oxy-m-phenylene-oxy(1,3-dioxo-1H-benz[de]isoquinoline-6,2(3H)-diyl)-p-phenylene-oxy-p-phenylene] (V)

To 37 ml of m-cresol was added, under a nitrogen atmosphere, 2.512 g (0.005 mole) of 1,3-bis(4-oxy-1,8-naphthalic anhydride)-phenylene, 1.001 g (0.005 mole) of oxydianiline, and .03% of isoquinoline. The mixture was slowly heated to 180°C and maintained at that temperature for 18 hours. The temperature was then increased to 202°C and maintained at that temperature for three hours. The reaction mixture was cooled to room temperature and precipitated into methanol. The polymer was collected, washed with methanol, dried under reduced pressure, and reprecipitated from methane sulfonic acid. The polymer 3.7 g (100%) had an intrinsic viscosity of 0.20 as determined in sulfuric acid and a Tg of 260°C (DSC).

Analysis-Calcd for $(C_{42}H_{22}O_7N)_n$ (percent): C, 75.70; H, 3.33; N, 4.20

Found (percent): C, 72.96; H, 3.04; N, 4.22

- f. Poly[(1,3-dioxo-1H-benz[de]isoquinoline-2,6(3H)-diyl)thio-m-phenylene-thio(1,3-dioxo-1H-benz[de]isoquinoline-6,2(3H)-diyl)-p-phenyleneoxy-p-phenylene] (VI)

A solution containing 0.3057 g (0.00153 mole) of oxydianiline, 0.8154 g (0.00153 mole) of 1,3-bis(4-thio-1,8-naphthalic anhydride)-phenylene, and 0.08 g of isoquinoline dissolved in 12 ml of m-cresol was heated, under a nitrogen atmosphere, for 20 hours at 180-200°C. The reaction mixture was allowed to cool to room temperature and the polymer was precipitated into 1.5 liters of methanol. The polymer was collected and washed several times with methanol and air-dried to give 1.04 g (97%) which had an inherent viscosity of 0.26 dl/g in sulfuric acid (0.5 g/100 ml at 30°C) and a Tg of 253°C (DSC).

Analysis-Calcd for $(C_{42}H_{22}O_5N_2S_2)_n$ (percent): C, 72.19; H, 3.17; N, 4.01;

S, 9.18

Found (percent): C, 71.21; H, 2.97; N, 4.06;

S, 8.68

- g. Poly[(1,3-dioxo-1H-benz[de]isoquinoline-2,6(3H)-diyl)oxy-4,4'-diphenyl-sulfideoxy(1,3-dioxo-1H-benz[de]isoquinoline-6,2(3H)-diyl)-p-phenyleneoxy-p-phenylene] (VII)

A solution containing 0.5058 g (0.0025 mole) of oxydianiline, 1.564 g (0.0025 mole) of 4,4'-bis(4-oxy-1,8-naphthalic anhydride)-diphenylsulfide, and 0.16 g of isoquinoline dissolved in 20 ml of m-cresol was heated, under a nitrogen atmosphere, for 20 hours at 180-200°C. The cooled reaction mixture was poured into 1.5 liters of methanol to precipitate the polymer. The product was collected and washed several times with methanol and air-dried to give 1.45 g (75%) which had an inherent viscosity of 0.30 dl/g in sulfuric acid (0.5 g/100 ml at 30°C). The polymer exhibited a Tg of 269°C (DSC).

Analysis-Calcd for $(C_{48}H_{26}O_7N_2S)_n$ (percent): C, 74.41; H, 3.38; N, 3.62; S, 4.14
Found (percent): C, 72.55; H, 3.16; N, 3.25; S, 4.07

- h. Poly[(1,3-dioxo-1H-benz[de]isoquinoline-6,2(3H)-diyl)-oxy-4,4'-diphenylsulfoneoxy(1,3-dioxo-1H-benz[de]isoquinoline-6,2(3H)-diyl)-p-phenyleneoxy-p-phenylene] (VIII)

A solution containing 0.5008 g (0.0025 mole) of oxydianiline, 1.606 g (0.0025 mole) of 4,4'-bis(4-oxy-1,8-naphthalic anhydride)-diphenylsulfone, and 0.16 g of isoquinoline dissolved in 20 ml of m-cresol was heated, under a nitrogen atmosphere, at 180-200°C for 20 hours. The cooled reaction mixture was poured into 500 ml of methanol to precipitate the polymer. The product was collected, washed several times with methanol, and air-dried to give 2.0 g (99%) which had an inherent viscosity of 0.29 dl/g in sulfuric acid (0.5 g/100 ml at 30°C). The polymer exhibited a Tg of 317°C (DSC).

Analysis-Calcd for $(C_{48}H_{26}O_9N_2S)_n$ (percent): C, 71.46; H, 3.25; N, 3.47;
S, 3.97
Found (percent): C, 68.77; H, 3.01; N, 3.18;
S, 4.15

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